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Anodic behaviour of α-PbO$_2$ substrates containing different percentages of lower lead oxides

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A study has been made of the anodic behavior of lead oxide deposits containing 92, 80 and 60% α-PbO$_2$. The non-porous deposits were prepared by electrodeposition from a plumbite bath containing different proportions of 30% formaldehyde solution, acting as a reductant in the cases of 80 and 60% α-PbO$_2$. Measurements of the steady-state oxygen evolution reaction under constant surface conditions of the electrodes, were carried out galvanostatically within the current-density range 30–190 μA cm^{-2}. The oxygen overpotential values were found to increase with increasing the amount of superficially formed β-PbO$_2$ during anodization in sulphuric acid solution. In the proposed mechanism for the o.e.r, the rate determining step is an electron-transfer reaction. Tafel slopes having values of 220 ± 10 mV dec^{-1} were obtained. Possible interpretation of these higher slopes is given which is based on the dual barrier model. Potential-time decay curves reveal a retarded oxygen diffusion process.

1. Introduction

The structure of the lead dioxide electrode plays an important role in the performance of lead-acid batteries. Variations of the Pb/O ratios of the lead dioxide lattice, α-, and β-PbO$_2$ ratios and the introduction of crystal modifying additives are all significant factors which influence the lifetime as well as the capacity of the positive plates. Also, the structure of the positive plate developing during cycling is a function of such factors as current density, gas formation, rate and habit of crystal growth as well as the mode of operation.

Lead dioxide exists in two crystalline modifications, α-PbO$_2$ which is orthorhombic and β-PbO$_2$, which is tetragonal. Without loading, the pure α-PbO$_2$ is more stable than the pure β-PbO$_2$ in acid solutions with pH > 1. This was shown [1] by measuring the potential of these two electrodes as a function of the pH of the solution. For pH values lower than 1, i.e. in strongly acidic solutions, the reverse is true and β-PbO$_2$ is more stable than α-PbO$_2$. This crossover in stability of the two crystallographic forms of PbO$_2$ is of importance from the practical point of view in the lead-acid battery as it was observed that newly formed positive plates usually show more α-PbO$_2$ in their interior than in their surface layers.

The pure PbO$_2$ electrode is known to be a very good conductor with electrons as charge carriers; this good conductivity may be due to oxygen deficiency [2]. It appears that in many cases the oxygen content of α-PbO$_2$ is less than that of β-PbO$_2$ [3]. If oxygen deficiency is the cause of the conductivity of PbO$_2$, the α-form should be a slightly better electronic conductor than the β-form. This conclusion is in accordance with the NMR measurements of Frey and Weaver [4]. However, these findings are not in agreement with earlier Hall coefficient measurements [5] which showed that the conductance is dependent upon the Pb/O ratios and that it decreases with decreasing the oxygen content of lead dioxide. Variation of the Pb/O ratio is known to be accompanied by phase

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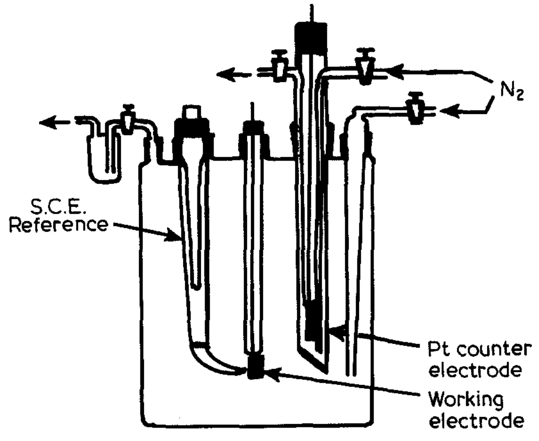
change and lower oxides, namely PbO, Pb_3O_4, and Pb_2O_3, are formed, which are poor electronic conductors [6].

The aim of this work was to investigate the electrochemical behaviour of electrodeposited α-PbO_2 electrodes containing different percentages of lower lead oxides in 0·1 M H_2SO_4 solution. This is carried out by following the polarization characteristics of these deposits under galvanostatic conditions using relatively low current densities. The influence of the lower oxides on the oxygen evolution reaction at the PbO_2 surface was also investigated.

2. Experimental

The chemicals used in this investigation were A. R. grade (B. D. H. and Merck), and all solutions were prepared from doubly distilled water.



Polarization cell

The electrolytic cell was made of Pyrex glass with a capacity of about 250 ml and was air thermostated at 30°C. The counter as well as the reference electrodes were separated from the main electrolyte through sintered glass disks (G4). The end of the reference electrode was elongated in the form of a Haber-Luggin capillary, which was placed at a distance of about 0·1 mm from the working electrode. The counter electrode was a platinum sheet with an area of 10 cm^2. The reference electrode was a saturated calomel electrode, E_h = 238 mV (T = 303 K).

The working electrodes were prepared by electrodeposition on platinum sheets having surface areas of 2 cm^2. The electrolytic bath for the deposition of the lead dioxode electrodes was obtained by preparing a stock solution, under an atmosphere of purified nitrogen, having the following composition: 500 ml of carbonate-free saturated potassium hydroxide solution, 500 ml of saturated sodium acetate solution, 100 ml of saturated lead acetate solution and 500 ml bidistilled water. The electrolysis was carried out in a cell with two compartments separated by a sintered glass disk (G4).

Depending upon the presence or absence of the reducing agent and its amount, the following electrodeposited oxides were obtained:

2.1. *92% α-PbO_2 deposit*

In this case the electrolysis was carried out without adding the reducing agent. The applied cell potential was adjusted at a value of 4 V such that a constant current density (c.d.) of 25 mA cm^{-2} passed through the cell. This c.d. was applied for 1–2 min. The cell potential was then changed to about 2 V and the anodic c.d. was readjusted to 1 mA cm^{-2} for 2 h. A strongly adhering greyish deposit was obtained. If the electrolysis was carried out under the starting conditions only, a thick spongy non-adherent deposit was obtained. On the other hand, carrying out the electrolysis at a comparatively low c.d., e.g. at 1 mA cm^{-2} using 2 V as the cell potential, oxygen evolution occurred without deposit formation.

2.2. *80% α-PbO_2 deposit*

In order to obtain deposits with decreasing α-PbO_2 contents, the solution of the plating bath was mixed with 30% formaldhyde solution, which acts as a reductant. The mixing ratio was 5:1 by volume for the stock solution to formaldhyde. The cell potential as well as the anodic c.d. were the same as in the case of the 92% α-PbO_2 deposit. The appropriate alkalinity for the electrolyte bath after adding the reductant was found to be within the range of 1·0–1·2 M. Under such conditions electrodeposition occurred smoothly leading to the formation of stronly adhering greyish deposits. For alkalinities lower than 0·8 M, separation of $Pb(OH)_2$ takes place and for higher values than 1·2 M, dissolution of the initially formed thin layer of the deposit occurs.

2.3. *60% α-PbO_2 deposit*

The electrolysis conditions were the same as above and the mixing ratio of the stock solution to the formaldhyde was 2·5:1·0 by volume. The suitable alkalinity of the plating bath was found to be within the range of 1·5–1·7 M. The deposits were smooth and lustrous.

According to Rüetschi *et al.* [1], the initially formed thin deposits have a non-porous structure. Determination of the α-PbO_2 contents of the deposits was carried out by the thiosulphate method described by Topf [7]; the results were reproducible within ± 1%.

X-ray diffraction examination of a specimen from the 92% α-PbO_2 deposits showed the presence of the lattice structure corresponding to PbO. However, the lines of PbO were relatively faint compared to those of α-PbO_2. The formation of PbO can be attributed to codeposition during anodic oxidation of the plumbite anion. The specimen corresponding to the 80% α-PbO_2 deposits showed, together with the lines of α-PbO_2, the presence of lines corresponding to Pb_2O_3 together with very few lines for the PbO. The 60% α-PbO_2 specimens showed lines similar to the 80% α-PbO_2; however, the lines corresponding to the Pb_2O_3 were more intense whereas those of PbO were very few.

The electrodes were thoroughly washed with bidistilled water until the washing solution became alkali free, and then washed with the electrolyte solution before being dipped in the oxygen-free electrolyte in the cell. Temperature fluctuations were avoided in order to prevent cracking of the deposited layer.

The method used in these measurements is the constant surface method recommended by Beck and Wynne-Jones [8] and modified later by Rüetschi *et al.* [1]. In this method, the electrodes were prepolarized at low current densities and then left on open circuit for 24 h prior to the application of the next higher c.d. In the present investigation, preanodization was carried out for 4 h at c.d.'s of 30, 50 and 80 $\mu A\ cm^{-2}$ for the 92, 80 and 60% α-PbO_2 electrodes, respectively. The amount of charge passing through the electrodes under such conditions is not sufficient for the oxidation of the whole substrate. After each anodization the electrode potential was allowed to decay to a value slightly above the reversible potential of the $PbO_2/PbSO_4$, 0·1 M H_2SO_4 system. In this manner, no $PbSO_4$ crystals are formed on the electrode surface and consequently there will be no change of the electrode surface area. During the measurements, purified nitrogen was allowed to flow over the electrolyte solution.

The currents were supplied from a self-made galvanostat and potentials were measured by a high-precision potentiometer (Muirhead D-972-A, England).

All measurements were carried out at 30°C; the potentials were referred to the reversible hydrogen electrode and the c.d. to cm^2.

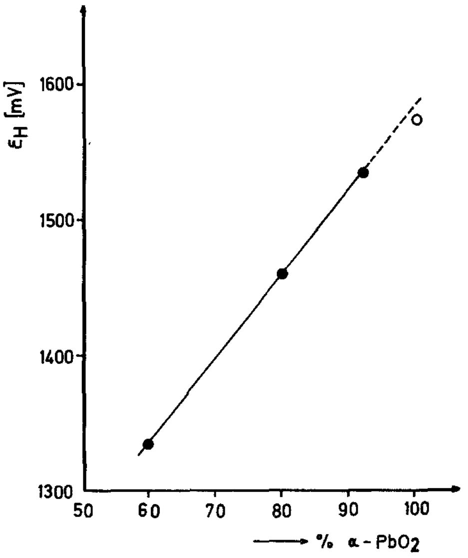


Fig. 1. Reversible potential at open circuit as a function of percentage of α-PbO_2 in the deposits in 0·1 M H_2SO_4 solution at 303 K. ● this work; ○ Rüetschi *et al.* [1]

3. Results

The reversible potentials at open circuit as a function of percentage of α-PbO_2 in the deposits, in 0·1 M H_2SO_4, are shown in Fig. 1. A straight line is obtained which on extrapolation to 100% α-PbO_2 gives a value for the reversible potential E_h = 1·582 V (T = 303 K). This value agrees satisfactorily with the value E_h = 1·572 V measured by Rüetschi *et al.* [1] on pure α-PbO_2 in the same solution and at the same temperature.

Fig. 2 shows the constant current build-up of potential with time for the anodic polarization of the 92% α-PbO_2 deposits in 0·1 M H_2SO_4 solution.

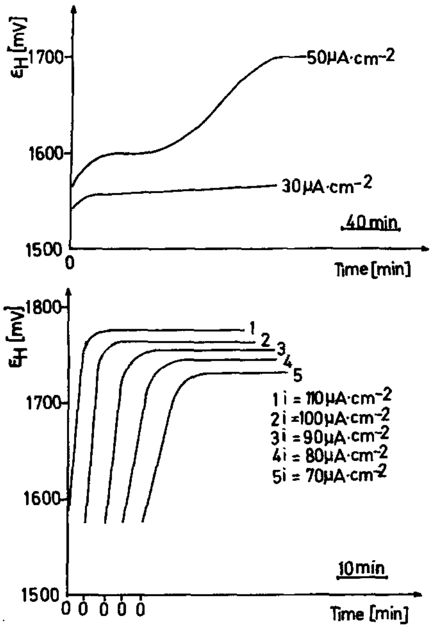


Fig. 2. Constant current build up of potential with time for the anodic polarisation of the 92% α-PbO_2 deposits in 0·1 M H_2SO_4 solution at 303 K.

On applying a c.d. of 30 μA cm^{-2}, the potential increases over a time period of a few min to a value about 10 mV higher than the reversible potential and then remains constant. At this potential, oxidation of the superficially formed $PbSO_4$ to β-PbO_2 takes place. (The formation of β-PbO_2 is favoured energetically under anodizing conditions [1].) At a c.d. of 50 μA cm^{-2}, the potential attains at first a steady state value, which corresponds to that of the $PbO_2/PbSO_4$ couple, and which extends for about 2 h. The potential then increases slowly to the oxygen evolution value. At the higher c.d.'s, the potential increases linearly with time in order to approach a steady state oxygen evolution value.

Fig. 3 illustrates the potential-time curves for the 80% α-PbO_2 deposits. These curves are similar to those obtained in the case of the 92% α-PbO_2 deposit. In this case, however, the pre-anodizing c.d. is higher than that in the case of the 92% α-PbO_2 deposits. This is due to the increased percentage of lower lead oxides which in turn increase the amount of the $PbSO_4$ formed on the electrode surface. Consequently, a higher c.d. is required for its oxidation to β-PbO_2.

The potential-time curves for the 60% α-PbO_2 deposits are given in Fig. 4. On applying an anodic

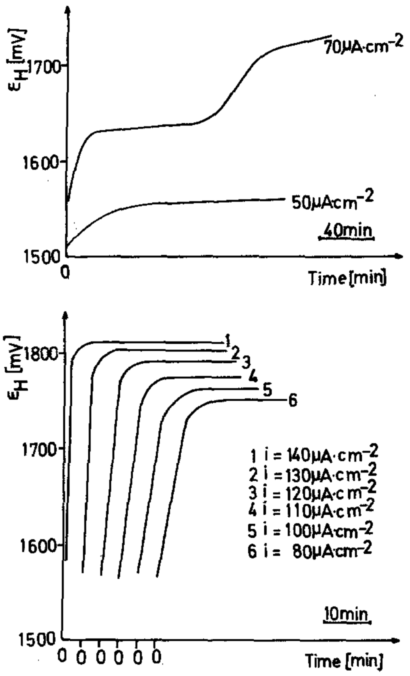


Fig. 3. Constant current build-up of potential with time for the anodic polarisation of the 80% α-PbO_2 deposits in 0·1 M H_2SO_4 solution at 303 K.

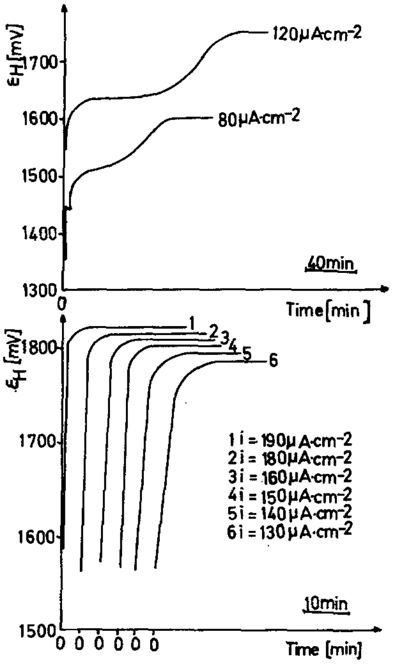


Fig. 4. Constant current build-up of potential with time for the anodic polarisation of the 60% α-PbO_2 deposits in 0·1 M H_2SO_4 solution at 303 K.

c.d. of 80 $\mu A\,cm^{-2}$, the curves attain two plateaux at about $E_h = 1500$ V and $E_h = 1580$ V respectively. The first plateau probably corresponds to the oxidation of the lower oxides or their disproportionation to $PbSO_4$ and PbO_2, whereas the higher one corresponds to the $PbO_2/PbSO_4$ couple. The maximum appearing at $E_h = 1{\cdot}450$ V may be attributed to a crystallisation process [9] occurring at the electrode surface after the charging of the double layer. At a c.d. of 120 $\mu A\,cm^{-2}$ a rapid rise in potential occurs after which a plateau is attained at $E_h = 1{\cdot}627$ V which corresponds to the $PbO_2/PbSO_4$ couple. This arrest extends over a period of about 2 h. The positive shift in potential (+ 50 mV) of the arrests obtained at the prepolarizing current and that at which oxygen evolution starts can be ascribed to adsorption of oxygen species in the latter case.

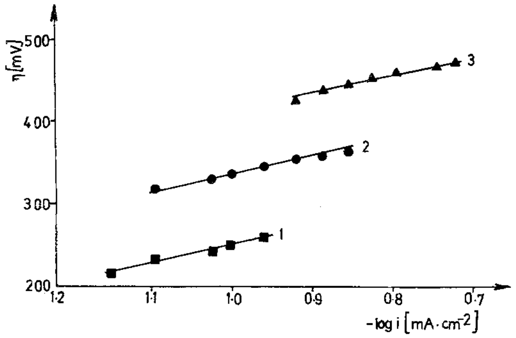


Fig. 5. Steady-state current-density overpotential curves of the oxygen evolution reaction in 0·1 M H_2SO_4 at 303 K. (1) 92% α-PbO_2 deposit; (2) 80% α-PbO_2 deposit; (3) 60% α-PbO_2 deposit.

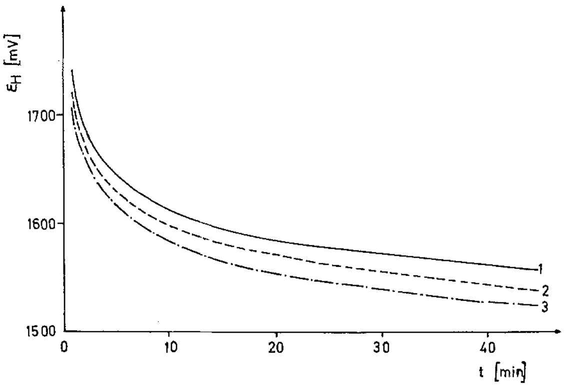


Fig. 6. Open circuit decay of potential with time in 0·1 M H_2SO_4 at 303 K. (1) 92% α-PbO_2 deposit, $i = 110\,\mu A\,cm^{-2}$; (2) 80% α-PbO_2 deposit, $i = 110\,\mu A\,cm^{-2}$; (3) 60% α-PbO_2 deposit, $i = 130\,\mu A\,cm^{-2}$.

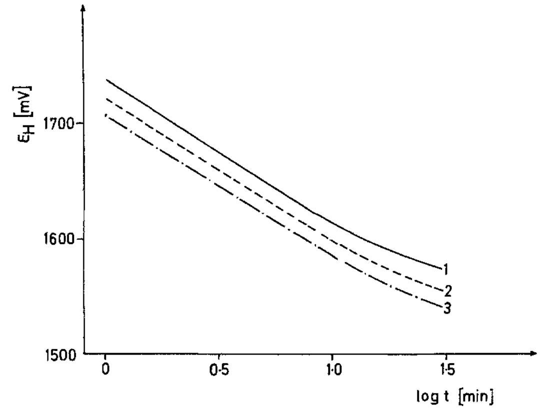


Fig. 7. Open circuit decay of potential with logarithm of time in 0·1 M H_2SO_4 at 303 K. (1) 92% α-PbO_2 deposit, $i = 110\,\mu A\,cm^{-2}$; (2) 80% α-PbO_2 deposit, $i = 110\,\mu A\,cm^{-2}$; (3) 60% α-PbO_2 deposit, $i = 130\,\mu A\,cm^{-2}$.

Fig. 5 illustrates the current density-overpotential curves for the oxygen evolution reaction obtained by anodic polarization of the 92, 80 and 60% α-PbO_2 deposits. The overpotential values were referred to the equilibrium potentials of the corresponding deposits in the same electrolyte. The straight lines obtained have a single slope in the cases studied, indicating that the process of oxygen evolution is governed by a single mechanism within the applied c.d. range. It can be seen also that the overpotential increases with decreasing the initial content of α-PbO_2 in the deposits. This can be ascribed to the increased amount of superficially formed β-PbO_2 as a result of the anodisation of the deposits in sulphuric acid solution [1]. The Tafel slopes obtained from these curves are almost the same within the limit of experimental error and have a value of $b = 220 \pm 10\,mV\,dec^{-1}$.

Representative open circuit decay of potential with time curves for all three types of deposits are shown in Fig. 6. In all cases the curves show a rapidly decreasing portion during the first few minutes followed by a region where the potential decreases slowly with time. Fig. 7 illustrates the plot of open circuit decay of potential versus log time for the three deposits. For times up to 10 mins, straight lines are obtained with a slope $dE/d\log t = -120 \pm 5\,mV\,dec^{-1}$. The value of the slope obtained is almost half the value for the potential build-up process. The deviation from linearity for $t > 10$ min is an indication that another process takes place at the electrode surface which is different from that which takes place in the first few minutes

4. Discussion

In the present work high Tafel slopes $b_+ =$ 220 ± 10 mV were obtained for the oxygen evolution reaction (oer). Similar observations with values for $b = 2{\cdot}303\ [(2RT/F)]$ were reported by several authors [10–15]. Such high slopes were explained in terms of a dual barrier-type postulate.

Assuming that the rate determining step in the oer is an electron transfer reaction occurring most likely during the discharge of H_2O molecules from acid solutions [16], then the mechanism can be represented as:

$$(H_2O)_{ads} \xrightarrow{RDS} (OH)_{ads} + H^+ + e \qquad (1)$$

followed by

$$2(OH)_{ads} \rightleftharpoons H_2O + (O)_{ads} \qquad (2)$$

$$(O)_{ads} + (O)_{ads} \rightleftharpoons (O_2)_{ads} \qquad (3)$$

$$(O_2)_{ads} \rightleftharpoons O_2. \qquad (4)$$

The anodic current density is then given by the following equation:

$$i = K_1 a_{H_2O} \exp\left(\frac{\alpha F E}{RT}\right), \qquad (5)$$

where a_{H_2O} is the water activity and E is the electrode potential measured with respect to the reference electrode. The value of the constant K_1 will depend on the particular reference electrode used. From Equation 5, one gets for the Tafel slope:

$$b_+ = \left(\frac{E}{\log i}\right)_{a_i} = 2{\cdot}303\left(\frac{RT}{\alpha F}\right)$$

$$= 118{\cdot}6\,\mathrm{mV}\ (\alpha = 0{\cdot}5 \text{ and } T = 298\,\mathrm{K}).$$

The fact that the experimental slope $b_+ =$ 220 ± 10 mV indicates that charge transfer cannot take place in such a simple manner.

It has been reported earlier, [17], that adsorption of SO_4^{2-} on a PbO_2 electrode surface can take place. Therefore, the oxygen overpotential on a PbO_2 electrode may be influenced by the amount of SO_4^{2-} anions adsorbed. However, the potential of zero charge (E_z) for PbO_2 in H_2SO_4 solutions as determined by several authors [18–22] was found to lie between $E_z = 1{\cdot}78$ and $E_z = 1{\cdot}90$ V within the concentration range 0·02–0·20 M H_2SO_4, solution and oxygen evolution takes place within the potential range 1·73 V up to 1·81 V, as can be seen in Figs. 2–4, then the excess specific adsorption of SO_4^{2-} anions is reduced to a minimum. Therefore, it can be assumed that the contribution of SO_4^{2-} anion adsorption to the oxygen overpotential is negligible. Therefore the barrier is unlikely to be attributable to SO_4^{2-} anion adsorption.

According to Kittel [5], using Hall coefficient measurements, the removal of oxygen from PbO_2 by thermal decomposition is accompanied by a decrease in conductivity and the removal of 13% of the oxygen initially present results in a 13·5 x decrease in the conductivity of the PbO_2. This decrease in conductivity is due to the formation of non- or less-conducting compounds. This is in accordance with the viewpoint of Burbank [22] and others that a new phase forms takes place at an O/Pb ratio of 1·90–1·95. The new phase has a lower concentration of free electrons than pure PbO_2 and its presence in the substrate of PbO_2 will form a barrier for electron transfer.

X-ray analysis of the deposits used in this investigation showed the presence of non- and less-conducting lower lead oxides. Also, the experiments were carried out under pre-anodization and charging conditions such that oxygen evolution takes place on deposits whose surface is oxidised to PbO_2 whereas its underlying substrate still containing lower oxides. The high Tafel slopes observed may be accordingly interpreted on the basis of the dual barrier model postulated firstly by Mayer [12] for cathodic studies carried out on a zirconium electrode covered with a film of ZrO_2.

The charge carriers (i.e. the electrons) must firstly surmount a potential E_b during its migration through the barrier and then a second potential E_s across the double-layer where the actual electrochemical charge transfer process takes place. Therefore, only a part of the total electrode potential E is responsible for the electrochemical charge transfer in the double layer [11].

Under steady-state conditions, which is the case in this work, the two potential-dependent reactions occur at an equal rate, which is given by:

$$i = K_b \pi (a_i)^{p_i} \exp\left(\frac{\alpha_b F E_b}{RT}\right) \qquad (6)$$

or

$$i = K_s \pi(a_j)^{p_j} \exp\left(\frac{\alpha_s F E_s}{RT}\right), \qquad (7)$$

where K_b = rate constant for the barrier reaction; K_s = rate constant for the charge transfer reaction across the double layer; α_b = transfer coefficient across the barrier; α_s = transfer coefficient across the double layer; $\pi(a_i)^{p_i}$ = the product of the activities of electrons, holes etc. in the barrier, i.e., the lower lead oxide substrate; $\pi(a_j)^{p_j}$ = the product of the activities of species taking part in the charge transfer in the double layer.

Taking into account that $E = E_b + E_s$, then it follows that:

$$i = K_b^{\alpha_s}[\pi(a_i)^{p_i}]^{\alpha_s} K_s^{\alpha_b}[\pi(a_j)^{p_j}]^{\alpha_b} \exp\left(\frac{\alpha_t F E}{RT}\right) \qquad (8)$$

where

$$\alpha_t = \frac{\alpha_b \alpha_s}{\alpha_b + \alpha_s}.$$

Setting $\alpha_b = \alpha_s = 0{\cdot}5$, then for a single electron transfer step the overall charge transfer coefficient $\alpha_t = 0{\cdot}25$ and from Equation 8 one gets for the Tafel slope $b_+ = 240$ mV. Thus the experimentally obtained Tafel slopes agree satisfactorily with those calculated from Equation 8 based on the dual barrier model.

The slopes of potential versus log time for the decay curves are different in sign and magnitude from those for the build-up curves. Taking into account that the electrode potential is a linear function of the surface concentration of oxygen and that the rate of oxygen evolution and desorption is an exponential function of the electrode potential [1, 24, 25], then it follows that:

$$i = -K_1 \frac{d[O]}{dt} = -K_2 \frac{dE}{dt} = K_3 \exp = \left(\frac{\alpha F E}{RT}\right), \qquad (9)$$

where $[O]$ is the surface concentration of oxygen. Integration of Equation 9 leads to:

$$t = -\frac{K_2}{K_3}\frac{RT}{\alpha F}\left[\exp\left(\frac{\alpha F E}{RT}\right) - \exp\left(\frac{\alpha F E_0}{RT}\right)\right], \qquad (10)$$

which can be written as:

$$E = E_0 - \frac{RT}{\alpha F}\ln t, \qquad (11)$$

where E_0 is the potential at the moment of circuit opening. From Equation 11, it follows that:

$$\frac{dE}{d\log t} = -2{\cdot}303\left(\frac{RT}{\alpha F}\right)$$
$$= -118{\cdot}6\,\text{mV}$$

which is in good agreement with the experimental results.

References

[1] P. Rüetschi, R. T. Angstadt and B. D. Cahan, *J. Electrochem. Soc.* **106** (1959) 547.
[2] U. B. Thomas, *ibid.* **94** (1968) 42.
[3] R.T. Angstadt, C. J. Venuto and P. Rüetschi, *ibid.* **109** (1962) 177.
[4] D. A. Frey and H. E. Weaver, *ibid.* **107** (1960) 930.
[5] A. Kittel, Dissertation Technische Hochschule, Prague, Czechoslovakia (1944).
[6] J. P. Hoare, 'The Electrochemistry of Oxygen', John Wiley and Sons, Inc. (1968), p. 243.
[7] K. Topf, *Z. Anal. Chem.* **26** (1944) 296.
[8] H. Beck and W. F. Wynne-Jones, *Trans. Faraday Soc.* **50** (1954) 136.
[9] W. J. Lorenz and A. A. El Miligy, *J. Electrochem. Soc.* **106** (1973) 1698.
[10] J. J. MacDonald and B. E. Conway, *Proc. Roy. Soc. (London)* **A269** (1962) 419.
[11] H. Gohr and E. Lange, *Z. Elektrochem.* **63** (1958) 673.
[12] R. E. Meyer, *J. Electrochem. Soc.* **107** (1960) 847.
[13] L. Young, Anodic Films, Academic Press Inc. New York, N.Y. (1961).
[14] B. E. Conway and A. K. Vijh, *J. Phys. Chem.* **71** (1967) 3637.
[15] A. K. Vijh and B. E. Conway, *Z. Anal. Chem.* **230** (1967) 81.
[16] J. P. Farr and N. A. Hampson, *Chemical Review,* **72** (1972) p. 702.
[17] I. G. Kiseleva and B. N. Kabanov, *Doklady Akad. Nauk SSSR* **108** (1956) 864.
[18] M. Steinberg and N. H. Nachttrieb, *J. Amer. Chem. Soc.* **72** (1950) 3558.
[19] I. G. Kiseleva, B. N. Kabanov and D. Leikis, *Dokl. Akad. Nauk SSSR* **49** (1954) 805.
[20] G. A. Kokarev, N. G. Bakhchsaraits' yan V. V. Panteleeva, *Tr. Mosk, Khim. Tkhnol. Inst.* **54** (1967) 161.
[21] D. I. Leikis and E. K. Ventrem, *Proc. Acad. Sci. USSR, Phys. Chem.* (Sect. Engl. Transl.) **112** (1957) 97.
[22] B. N. Kabanov, I. G. Kiseleva and D. I. Leikis, *Dokl. Akad. Nauk SSSR* **99** (1954) 805.
[23] J. Burbank, N.R.L. Report 6859, Naval Research Laboratory, Washington, D.C.
[24] E. Bears, *Marburger Sitzungsberichte* **63** (1928) 214.
[25] A. L. Pitman and G. W. Work, N.R.L. Report 5031, Naval Research Laboratory, Washington, D.C.